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Synthesis, characterization and optical properties of fluorinated poly(aryl ether)s containing phthalazinone moieties

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A series of novel fluorinated poly(aryl ether)s containing phthalazinone moieties (FPPEs) have been prepared by a modified synthetic procedure for optical waveguide applications. The obtained random copolymers exhibited excellent solubility in polar organic solvents, high glass transition temperatures (T_gs: 185–269 °C), good thermal stabilities (the temperatures of 1% weight loss: 487–510 °C) and good optical properties. By adjusting the feed ratio of the reactants, the refractive indices of TE and TM modes (at 1550 nm) could be well controlled in the range of 1.575–1.498 and 1.552–1.484, respectively. The optical losses of the FPPEs exhibited relatively low values (less than 0.27 dB/cm at 1310 nm). Additionally, the thermo-optic coefficient (dn/dT) values of the FPPEs at 1310 nm and 1550 nm (TE mode) ranged from -0.97×10^{-4} °C to -1.33×10^{-4} °C and from -0.96×10^{-4} °C to -1.29×10^{-4} °C, respectively.

1. Introduction

Polymer optical waveguides have attracted considerable attention for their possible application as optical components in optical communication systems due to their ease in processing, controllability of optical properties, and their cost-effective technology [1,2]. An optical waveguide generally consists of a waveguide core, in which the signal propagates, and a cladding, which surrounds the core and detains the optical signal inside the waveguide core. And it is essential for the core material to have a higher refractive index than the cladding in order to confine the light. Therefore, materials with a controllable refractive index are required for successful design and fabrication of photonic devices. Additionally, good film-forming properties, high thermal stability, and low optical losses in the near-infrared (IR) region of 1.0–1.7 μm, especially for the optical telecommunication wavelengths of 1.3 and 1.55 μm, are also required for materials used in optical applications [3,4]. However, most hydrocarbon-based polymers suffer from limited thermal stability and high optical propagation losses in the visible and near-IR region due to the vibrational overtone absorption of the C–H, O–H, and N–H bonds. A common method to minimize this kind of loss is to replace the C–H bonds by C–X (halogen) bonds in the result of their absorption overtones to longer wavelengths, thereby reducing the intrinsic optical loss in 1310 nm and 1550 nm. Work carried out in a number of laboratories has demonstrated that halogenations, particularly fluorination, could offer interesting opportunities for the alteration of properties such as refractive index, hydrophobicity and thermal stability. Thus a significant amount of research efforts have been performed on fluorinated or perfluorinated polymers such as fluorinated polyacrylates [5–7], fluorinated polyimide [8–12], perfluorocyclobutane [13–16], fluorinated dendrimer and hyperbranched polymers [17,18], fluorinated poly(arylene ether)s [19–22], and polysiloxanes and inorganic–organic hybrid polymers [23,24] for use as optical waveguide applications. Among them, fluorinated poly(arylene ether)s have exhibited the best integrated properties [4]. However, the conventional synthesis of those polymers, which is usually conducted by a nucleophilic aromatic substitution (S_NAr) polycondensation between aromatic dihalide and diphenol compounds in *N*,*N*′-dimethylacetamide (DMAc) with an excess of anhydrous potassium carbonate at high temperatures (e.g., 160 °C), prevalently leads to side reactions such as branching or cross-linking [25]. Consequently, continuous efforts on the synthesis of the new fluorinated polymers with facilely reactive conditions are still worth making for optical applications.

It is supposed that poly(phthalazinone ether)s will be particularly suitable to be used as potential polymeric optical materials after being partially fluorinated due to their relatively modest synthetic condition, extraordinarily high T_g (265–305 °C), excellent

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thermal stability and good thin film processability [26–29]. Herein, we reported the synthesis of novel fluorinated poly(aryl ether)s containing phthalazinone moieties (FPPEs) prepared by the modified polycondensation reaction.

2. Experimental

2.1. Materials

4-(4′-Hydroxyphenyl)phthalazin-1(2*H*)-one (DHPZ) was gifted by Dalian Polymer New Material Co. Ltd., PR China, and recrystallized in *N*,*N*-dimethylacetamide (DMAc), subsequently, it was dried in vacuum at 120 °C for 24 h before use. 4,4′-(Hexafluoroisopropylidene)diphenol (6F-BPA) and decafluorobiphenyl (DFBP) were purchased from Sigma–Aldrich and used without further purification. Analytical-grade anhydrous potassium fluoride (KF) and calcium hydride (CaH_2) (Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China) were used as received. Analytical-grade *N*,*N*′-dimethylacetamide (DMAc) (Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China) was purified by reduced pressure distillation prior to use, subsequently, the middle fractions were collected and stored over molecular sieves (Type 4 Å). All the other chemicals were of analytical-grade and purchased from Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China. And they were used without further purification unless otherwise noted.

2.2. Measurements

^{1}H NMR (400 MHz) and ^{19}F NMR (376 MHz) spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using $CDCl_3$ as a solvent and were listed in parts per million downfield from tetramethylsilane (TMS) and potassium fluoride (KF), respectively. Fourier transform infrared (FT-IR) spectra were recorded by reflection method with a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4 × 500 Å) arranged in series with THF as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. The glass transition temperatures (T_gs) were determined with a Mettler DSC822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C min^{-1} from 50 to 400 °C. Thermogravimetric analysis (TGA) of the polymers was performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} from 100 to 700 °C. Optical properties such as refractive index, optical loss and thermo-optic coefficient value (dn/dT) were measured by using a Sairon SPA-4000 prism coupler with the tolerance of ±0.0002.

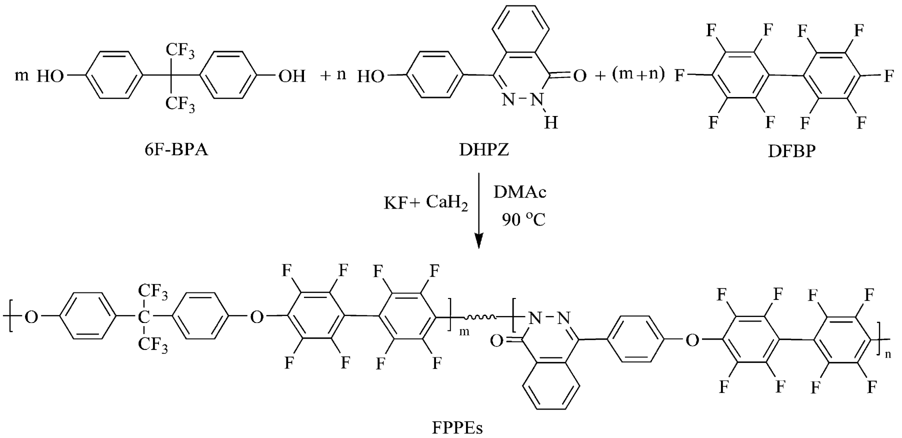
2.3. Polymer synthesis

A series of novel fluorinated poly(phthalazinone ether)s (FPPEs) were synthesized via a modified nucleophilic aromatic substitution (S_NAR) polycondensation reaction as illustrated in Scheme 1. A typical preparation of these polymers (FPPE-2) was illustrated as follows. Potassium fluoride (KF, 16 mmol) and calcium hydride (CaH_2, 40 mmol) were added to a solution of 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA, 15 mmol), 4-(4′-hydroxyphenyl)-phthalazin-1(2*H*)-one (DHPZ, 5 mmol) and decafluorobiphenyl (DFBP, 20 mmol) in 10 mL of anhydrous *N*,*N*′-dimethylacetamide (DMAc). Nitrogen was purged through the reaction mixture with stirring for 10 min, and then the mixture was slowly heated to 90 °C and kept at this temperature for 4 h. After cooling, the viscous solution was slowly poured into sufficient ethanol under vigorous stirring to precipitate the product. After filtered and dried, the polymer was purified by filtering its *N*,*N*′-dimethylacetamide (DMAc) solution through a thin layer of Celite545 (0.02–0.1 mm) before precipitating it into sufficient ethanol. The white powder was collected by filtration and then treated thoroughly with boiling pure water, followed by filtration, washing thoroughly with pure water and methanol, and then drying at 60 °C under vacuum for 24 h. The total yield of FPPE-2 was 91%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.06 (d, *J* = 8.5 Hz, 12H), 7.24 (d, *J* = 9.9 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 12H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.80–8.00 (3H, m), 8.63 (1H, m). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: −64.07 (20F, s), −136.61 (2F, m), −137.44 (16F, m), −143.31 (2F, m), −152.42 (16F, m). IR (film, cm^{-1}): 1696 (C═O), 1608, 1487 (aromatic ring), 1260, 1229 (aromatic ether bond).

The following polymers with different fluorine contents were prepared using the same procedure as outlined above and characterized as follows.

FPPE-1: 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.05 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: −64.09 (3F, s), −137.45 (2F, m), −152.37 (2F, m). IR (film, cm^{-1}): 1609, 1509, 1488 (aromatic ring, C═C), 1261, 1229 (C–O–C).

FPPE-3: 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.06 (d, *J* = 7.5 Hz, 4H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 4H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.75–8.00 (3H, m), 8.62 (1H, m). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: −64.07 (15F, s), −136.66 (4F, m), −137.41 (16F, m), −143.26 (4F, m), −152.44 (16F, m). IR (film, cm^{-1}): 1696(C═O), 1607, 1488 (aromatic ring, C═C), 1260, 1209 (C–O–C).



Scheme 1. Synthetic route of FPPEs.

FPPE-4: 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.06 (d, $J = 8.1$ Hz, 1.5H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 1.5H), 7.69 (d, $J = 7.8$ Hz, 2H), 7.80–8.00 (3H, m), 8.63 (1H, m). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: −64.07 (5F, s), −136.66 (2F, m), −137.43 (10F, m), −143.27 (4F, m), −152.40 (8F, m). IR (film, cm^{-1}): 1696(C=O), 1608, 1487 (aromatic ring, C=C), 1261, 1209 (C–O–C).

FPPE-5: 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.26 (d, $J = 5.5$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.75–8.00 (3H, m), 8.64 (1H, m). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: −136.67 (1F, m), −137.41 (3F, m), −143.24 (2F, m), −152.46 (2F, m). IR (film, cm^{-1}): 1689(C=O), 1605, 1488 (aromatic ring, C=C), 1259, 1209 (C–O–C).

2.4. Film preparation and optical properties measurements

The substrates used in the experiments were highly polished Si/SiO_2 wafers. Organic residues on the silicon surfaces were removed by the successive ultrasonic cleaning with acetone, alcohol and ion free pure water. The polymers were dissolved in cyclohexanone at a concentration of 20 wt%. Then the solution was filtered through a 0.45 μm Teflon microfilter and spin-coated on a Si/SiO_2 substrate. The spin-coating speeds ranged from 1000 to 6000 rpm. And the spinning time was 30 seconds. In order to guarantee the quality of the spin-coated films, the whole spin-coating procedure was carried out in a 1000 class ultraclean room. The resulting films were dried at 60 °C (30 min) and 120 °C (4 h) to remove the residual solvent under vacuum. The refractive indices of the polymer films were measured by using a Sairon SPA-4000 prism coupler at the wavelengths of 1310 nm and 1550 nm with the tolerance of ±0.0002. The optical losses of the polymer films were measured on slab waveguide samples using the high-index liquid immersion technique on a Sairon SPA-4000 prism coupler, which gave a precise measurement down to 0.05 dB/cm [30,31]. In this technique, light was coupled to a slab waveguide by prism coupling. After propagating a certain distance, the light was out-coupled from the waveguide by immersing it into the liquid oil with an index of refraction slightly higher than that of the film (herein, the refractive index of the oil was 1.60.). And the propagation loss could be calculated with the out-coupled intensity of the guided light described as a function of the propagation distance.

3. Results and discussion

3.1. Synthesis of FPPEs

Traditionally, non-fluorinated poly(arylene ether)s are prepared by the polycondensation of a bisphenol with an activated aromatic dihalide in an aprotic polar solvent, such as DMAc, in the presence of a base, such as K_2CO_3, at high temperatures, such as 160 °C. However, following this polymerization condition, there must exist side cross-linking reactions in the polycondensation reaction of bisphenols and perfluorinated monomers, such as decafluorobiphenyl, because of the high reactivities of other fluorine atoms except the *para*-position fluorine atoms. Recently, potassium fluoride and calcium hydride were used as the catalyst and base in preparation of highly fluorinated poly(arylene ether)s. Compared with the conventional S_NAr polycondensations, the new approach could facilitate the formation of the phenolates and enable the polymerization to be performed at a low temperature, thereby suppressing most side reactions such as cross-linking and hydrolysis [22]. By the same token, potassium fluoride (KF) instead of K_2CO_3 was used to activate the phenol in our study. The synthetic route of fluorinated poly(aryl ether)s containing phthalazinone moieties (FPPEs) is illustrated in Scheme 1. In this reaction, potassium fluoride acted as a catalyst to convert the phenol group to the phenolate. Additionally, as reported previously [32], it also acted as a base to combine with HF to form a KHF_2 complex and precipitate it out of the solution, thereby promoting the polymerization reaction. Meanwhile, the neutralizing effect could also be achieved by the use of CaH_2. Using this approach, no water was generated, and as a result azeotropic distillation was no longer required, which lead to a more modest and lower temperature for the polymerization. It should be noted that the inorganic salts used in this reaction should be eliminated completely during the purifying process to avoid the undesirable optical loss. The purification of the resulting polymers involved filtering their DMAc solutions through the Celite layer before precipitating them into sufficient ethanol, collected by filtration and boiling in pure water, followed by filtration, washing thoroughly with pure water and methanol.

By changing the feed ratio of the DHPZ to the 6F-BPA, the fluorine content of FPPEs could be easily controlled, and there were totally five FPPEs with different fluorine contents prepared in this study (Table 1).

GPC analysis, using THF as the eluent and polystyrene as standards, revealed that the number-average molecular weights (M_ns) and polydispersities (M_w/M_ns) of FPPEs were in the range of 18,100–59,700 and 2.46–3.06, respectively, as summarized in Table 1.

3.2. Characterization of FPPEs

The chemical structures of the copolymers were characterized by ^{1}H NMR, ^{19}F NMR, and FT-IR spectra. By comparing the peaks of the copolymers in ^{1}H NMR spectra, as shown in Fig. 1, with the change of the ratio of the 6F-BPA units to DHPZ units in the copolymers, we were able to identify the peaks related to the phthalazinone segment (DHPZ) and bisphenol segment (6F-BPA). As illustrated in Fig. 1(a), the peak around 8.6 ppm was attributed to the H_e signal of phthalazinone, owing to the deshielding ring current effect of adjacent lactam. This downfield signal is the typical signal in all the phthalazinone derivatives and a good starting point to the assignment of the other atoms. Thus the chemical shift assignments of relative protons in our copolymers are listed in Fig. 1 and are consistent with the supposed polymer structures. It could be seen that the intensities of signals of phthalazinone segment proportionally increased with the feed

Table 1
Results of polymerization

Polymers	6F-BPA content[a] (mol%)	DHPZ content[b] (mol%)	DHPZ content from ^{1}H NMR[c] (mol%)	DFBP content[d] (mol%)	M_n[e] ($\times 10^4$)	M_w[e] ($\times 10^4$)	M_w/M_n[e]
FPPE-1	100	0	0	100	5.89	17.65	2.99
FPPE-2	75	25	23.6	100	5.97	14.93	2.50
FPPE-3	50	50	49.2	100	3.39	9.35	2.76
FPPE-4	25	75	74.2	100	1.81	4.55	2.46
FPPE-5	0	100	100	100	2.13	6.54	3.06

[a] Feed molar ratio of 6F-BPA relative to the total bisphenols.
[b] Feed molar ratio of DHPZ relative to the total bisphenols.
[c] Feed molar ratio of DFBP relative to the total bisphenols.
[d] The molar ratio of DHPZ relative to the total bisphenols in the copolymer chain was calculated with Eq. (1).
[e] M_n, M_w and M_w/M_n values were determined by GPC in THF with PS as a standard.

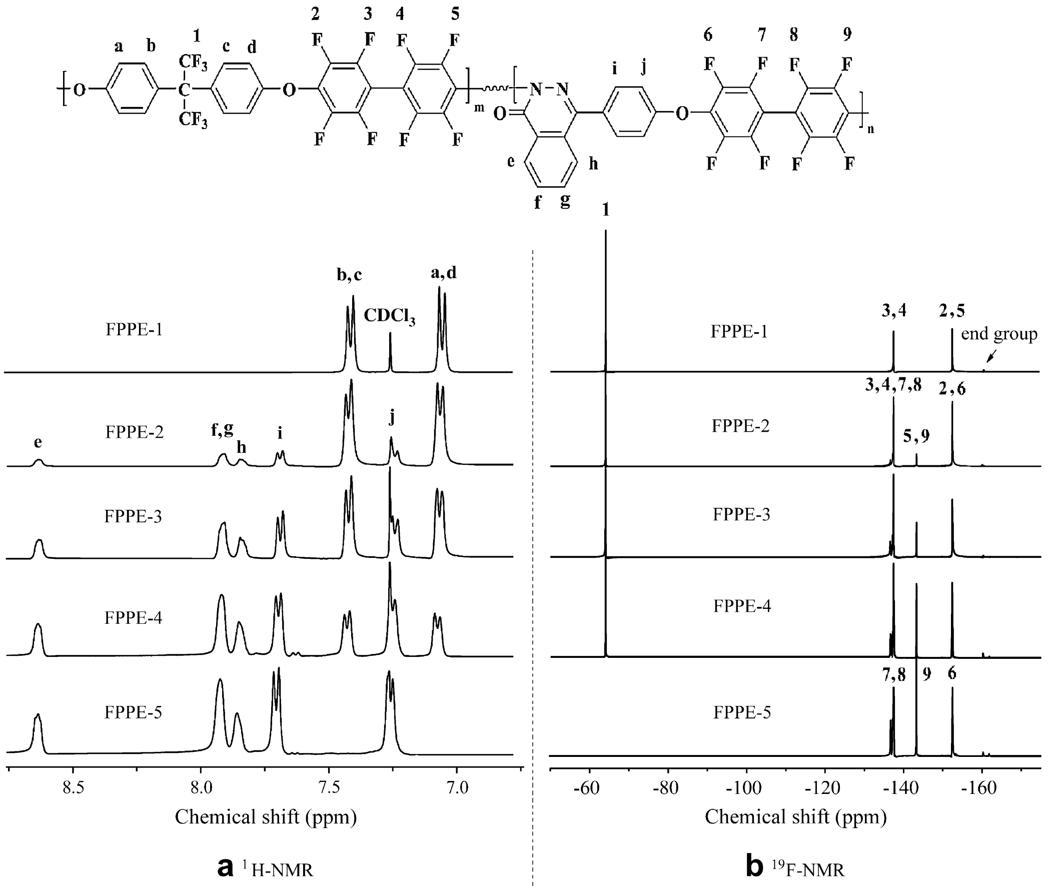


Fig. 1. (a) Partial ^{1}H NMR and (b) ^{19}F NMR spectra of FPPEs.

ratio of DHPZ to 6F-BPA and the peaks of bisphenol 6F-BPA decreased accordingly. It should be noted that, as described in Scheme 1, DHPZ is an asymmetric monomer and has two different reactive groups –N–H and –O–H. So we can see two peaks 6 and 9, which were attributed to F_6 adjacent to –O– and F_9 adjacent to –N– of lactam, respectively, in the ^{19}F NMR spectrum of FPPE-5, while only one peak in accord with F_2 and F_5 appeared in the homogeneous copolymer FPPE-1 from the reaction of 6F-BPA and DFBP (see Fig. 1(b)) because of the symmetric structure of 6F-BPA. Based on the above discussion, the intensity of fluorine signal adjacent to C–O–C is higher than that adjacent to C–O–N in the copolymers. On detailed examination of the ^{19}F NMR spectrum of FPPE-3, when the feed ratio of 6F-BPA and DHPZ was 1:1, the integral intensity of the peaks of F_2 and F_6 was three times that of the signal of F_5 and F_9. Additionally, all of the IR spectra of FPPEs showed the characteristic absorption bands near 1690 cm^{-1} (C=O stretching), 1605 cm^{-1}, 1488 cm^{-1} (C=C stretching vibration of the aromatic ring), 1260 cm^{-1} and 1210 cm^{-1} (Ar–O–Ar stretching). These characteristic bands in IR spectra correlated sufficiently well with the expected structure of the target substance. In addition, no peak attributed to branch structure existed in the ^{19}F NMR (Fig. 1(b)) spectra, indicating that a good control of the structure for FPPEs was realized under this polycondensation reaction condition.

Furthermore, since these two groups of peaks are well distinguished in the ^{1}H NMR spectra of FPPEs (see Fig. 1(a)), it is possible to determine the content of phthalazinone (depicted as DHPZ) segment in the copolymer chain using the following equation:

$$\text{DHPZ content}\% = \frac{I_{\mathrm{He}}}{I_{\mathrm{He}} + (I_{\mathrm{Hb}} + I_{\mathrm{Hc}})/4} \times 100\% \qquad (1)$$

where, the DHPZ content is the molar ratio of phthalazinone segment (DHPZ) relative to the total bisphenols, I_{He} is the intensity of the H_e signal, I_{Hb} and I_{Hc} is the intensity of H_b signal and H_c signal, respectively. And the calculated results are summarized in Table 1. It confirmed that the components of the obtained copolymers were reasonably close to the designed scales. Thus the feed molar ratio of DHPZ relative to the total bisphenols, that is, the molar sum of DHPZ and 6F-BPA, is used to characterize the relationship between T_gs, reflective indices, and its real content of the copolymers in this manuscript.

3.3. Solubility and thermal properties of FPPEs

The resulting polymers exhibited excellent solubility in polar organic solvents such as THF, $CHCl_3$, cyclohexanone, DMAc, DMF, NMP at room temperature, which makes them easier for film preparation and device fabrication. Besides the effect of fluorination, the excellent solubility of FPPEs could be ascribed to the phthalazinone structure and the flexible ether linkages. Though the phthalazinone moieties in the polymers were aromatic and rigid, there was a dihedral angle between phthalazinone and the attached phenyl group. This asymmetric and non-coplanar formation made polymers' chains twist, which helped to cumber the close packing of the polymers' chains, enlarge the average intermolecular distance of the polymers and enable solvent molecules to diffuse easily into the polymers' chains [33].

The glass transition temperatures (T_gs) of FPPEs were evaluated by DSC, which were conducted at a heating rate of 10 °C min^{-1} in nitrogen from 50 to 400 °C, and the results are summarized in Table 2. The DSC heating scans revealed only one distinct T_g in the range of

Table 2
Optical and thermal properties of FPPEs

Polymers[a]	Film thickness[b] (μm)	n_{TE}[c]	n_{TM}[c]	Optical loss[d] (dB/cm)	T_g[e] (°C)	$T_d^{1\%}$[f] (°C)
FPPE-1	3.03	1.4996	1.4860	0.173	185	503
FPPE-2	2.97	1.5321	1.5120	0.270	212	500
FPPE-3	2.98	1.5392	1.5151	0.169	234	492
FPPE-4	2.91	1.5521	1.5296	0.146	249	487
FPPE-5	2.93	1.5750	1.5521	0.210	269	510

[a] The sample codes were the same as shown in Table 1.
[b] The average value of film thickness, which was tested at four different points per film.
[c] Refractive index of the TE mode or TM mode at 1310 nm.
[d] Measured on slab waveguide samples using the high-index liquid immersion technique at 1310 nm.
[e] Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen.
[f] Thermal decomposition temperature, defined as the temperature of 1% weight loss, at a heating rate of 20 °C min^{-1} in nitrogen.

185–269 °C for the resulting copolymers. According to Fox equation, the T_gs of FPPEs could be predicted based on the feed ratio of the monomers as presented in Fig. 2 using Eq. (2):

$$\frac{1}{T_g} = \frac{Wt_1}{T_{g1}} + \frac{Wt_2}{T_{g2}} \tag{2}$$

where T_g is the glass transition temperature of the copolymer, Wt_1 is the weight fraction of 6F-BPA relative to the total bisphenol, Wt_2 is the weight fractions of DHPZ relative to the total bisphenol, T_{g1} and T_{g2} are the glass transition temperatures of the homopolymers derived from 6F-BPA with DFBP ($T_{g1} = 185$ °C) and from DHPZ with DFBP ($T_{g2} = 269$ °C), respectively. Fig. 2 displays the measured T_g and the predicted trend line according to the Fox equation. It could be seen from Fig. 2 that the T_g values of FPPEs increased from 185 to 269 °C when the content of DHPZ increased from 0 to 100 mol%. A good agreement of the T_gs of FPPEs with values predicted by the Fox equation according to the feed ratios was also observed. It was obvious that the variation of the copolymers' T_g values with DHPZ content approximately fitted the rule of random copolymers. These relatively higher T_g values in comparison with those of fluorinated poly(aryl ether)s [22,25,34] were also owing to the introduction of phthalazinone structure in the backbone, which hindered the movement of the main chains [29].

The thermal decomposition temperatures (T_ds), defined as the temperature of 1% weight loss, at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere, were also measured by TGA as shown in Table 2. The temperatures of 1% weight loss were in the range of 487–510 °C, which was high enough for optical applications [3].

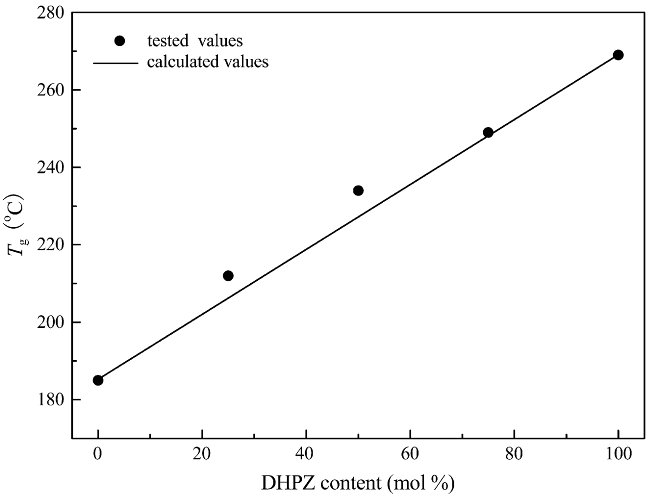


Fig. 2. Correlation between T_g of FPPEs and the DHPZ content (mol% relative to the total bisphenols): (●) experimentally determined T_g values from DSC. The solid line represents the calculated values according to the Fox equation.

3.4. Optical properties

Based on the device design and waveguide geometry, the polymer used as the core material must have a higher refractive index than that of the cladding material [35]. Thus fine-tuning of materials' refractive index is exceedingly important for their optical waveguide applications. The Lorentz–Lorenz equation, which is usually used to design high refractive index plastic lenses [36], shows the relationship between refractive index and molecular structure:

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{[R_D]}{M} \times \rho = \frac{[R_D]}{V} \tag{3}$$

where n_D is refractive index, M is molecular weight, ρ is density, V is molecular volume, and R_D is molecular refraction.

From Eq. (3), the following expressions for the refractive index can be easily derived:

$$n_D = \sqrt{\frac{1 + 2[R_D]/V}{1 - [R_D]/V}} \tag{4}$$

It is obvious that larger density, larger molecular refraction, and smaller molecular volume lead to larger refractive index, on the base of Eq. (4). Aromatic ring, halogen atoms except fluorine, sulfur atom, and heavy metal atoms are effective on increasing refractive indices.

The refractive indices of the FPPEs were measured by using the prism-coupling method on thin films. Fig. 3 shows the refractive indices (both the values of transverse electric mode and transverse magnetic mode, n_{TE} and n_{TM}) of the FPPEs at 1550 nm. By adjusting the DHPZ content from 100 mol% to 0 (relative to the total bisphenols), thereby increasing the fluorine content, the refractive indices of TE and TM modes decreased from 1.575 to 1.498 and from 1.552 to 1.484, respectively. The decrease of refractive indices attributed to the smaller electronic polarizability and larger free volume of the C–F compared to C–H bonds. The linear dependency of their refractive indices on the reactant content allowed the control of the refractive indices of the FPPEs.

Unlike silica glass, whose birefringence ($\Delta n = n_{TE} - n_{TM}$) arises from the stress formed in processing, the birefringence of polymer materials comes mainly from the preferred orientation of rigid groups and polymer chains [37]. In addition, a polymer film usually undergoes molecular orientation during spin-coating. From Table 2 it is observed that the birefringence of the FPPEs increased with

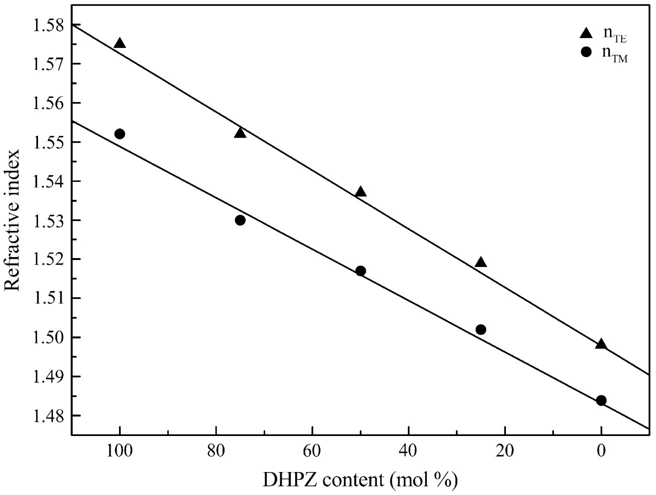


Fig. 3. Dependence between refractive index and DHPZ content (mol%) at 1550 nm.

increasing DHPZ content. The increase of birefringence attributed to the increase of the more rigid phthalazinone structure of DHPZ compared to the 6F-BPA units in the polymer chains. However, it should be noted that the birefringence in this system ($\sim$0.02), which was related to the optical anisotropy of the polymer material, was still a little higher. Although the large birefringence of a polymer film can find some applications, the birefringence still needs to be suppressed for the most applications of optical waveguides. Some further structural modifications, such as inserting cross-linkable units into the polymers, should be explored. In our previous study [37], it has been revealed that inserting cross-linking groups such as tetrafluorostyrene groups could effectively reduce the birefringence of the polymer. It could be ascribed to the reduction of electronic polarizability in the polymer chains. It has been proved that [38], birefringence depends on the polarizability and van der Waals volume of the repeating unit. Larger polarizability leads to high birefringence. During thermal cross-linking, the reaction of tetrafluorostyrol units leads to the break of π-conjugation, and consequently, results in a decrease in electronic polarizability of the polymer chains. As a result, a decrease in birefringence was observed. And such cross-linkable fluorinated polymers are currently under way in our group.

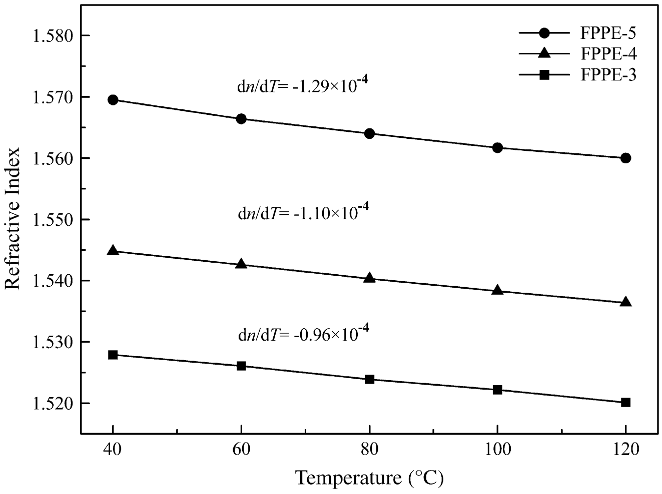


Fig. 4. Dependence between refractive index and temperature at 1550 nm (TE mode): (■) FPPE-3; (▲) FPPE-4; (●) FPPE-5.

Low optical loss in the infrared region is one of the key requirements of optical waveguides materials. It is well known that replacement of C–H units by C–F units is an efficient way to increase the optical transparency of a polymeric material in the near-infrared telecommunication windows (1.3 and 1.55 μm). The optical losses of FPPEs were evaluated from the slab waveguide loss using high-index liquid immersion method, and the results are summarized in Table 2. These polymers were observed to have very low optical losses at 1310 nm. For FPPE-4 and FPPE-3, the optical losses were 0.146 and 0.169 dB/cm, respectively, whereas those for FPPE-5 and FPPE-2 were 0.210 and 0.270 dB/cm, respectively. These relatively low optical losses of the polymers could be ascribed to the replacement of C–H units by C–F units which could shift the associated vibrational overtone to longer wavelengths, thereby increasing the optical transparency in the near-infrared communication region.

Besides refractive index and optical loss, an important property of polymers is that they have a large negative thermo-optic coefficient (dn/dT) which is 10–40 times larger (in absolute value) than that of more conventional optical materials such as glass, resulting in low-power-consumption thermally-actuated optical elements [39]. Fig. 4 shows the refractive indices of FPPE-3, FPPE-4 and FPPE-5 at different temperatures at the wavelength of 1550 nm (TE mode). The slopes of the curves represented the dn/dT values of the polymers. It could be seen that the refractive indices decreased linearly with increasing temperature, namely, all the polymers had a negative temperature coefficient of the refractive index. The dn/dT values of the FPPEs at 1310 nm and 1550 nm (TE mode) ranged from -0.97×10^{-4} °C to -1.33×10^{-4} °C and from -0.96×10^{-4} °C to -1.29×10^{-4} °C, respectively. As is known that a large T–O coefficient corresponds to a small temperature change, and thus small power input is needed for causing the necessary change in the refractive index of polymer waveguides. The dn/dT values of FPPEs, which are one order of magnitude larger than those of inorganic glasses [34], are especially useful for devices in which thermal jump actuation is utilized for switching optical communication signals from one optical circuit to another [2].

4. Conclusions

A series of novel fluorinated poly(aryl ether)s containing phthalazinone moieties have been designed and synthesized by the modified synthetic procedure. The obtained random copolymers exhibit excellent solubility in some polar organic solvents and high thermal stability, which could simplify device fabrication and processing. By adjusting the feed ratio of the reactants, the refractive indices could be well controlled. The optical losses of the FPPEs exhibited relatively low values (less than 0.27 dB/cm at 1310 nm). Additionally, the thermo-optic (T–O) coefficient (dn/dT) values of the FPPEs at 1310 nm and 1550 nm (TE mode) ranged from -0.97×10^{-4} °C to -1.33×10^{-4} °C and from -0.96×10^{-4} °C to -1.29×10^{-4} °C, respectively, which are one order of magnitude larger than those of inorganic glasses. These results indicate that the application of FPPEs in the field of optical waveguide appears feasible and promising.

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